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(54) Corrosion inhibitors

(57) A corrosion inhibitor comprises particles of an organic anion-exchange resin having nitrite anions chemically bound thereto. Protective coatings, for example, paints based on epoxy resins, alkyd resins, vinyl resins or chlorinated rubbers, may contain the particles in amounts up to 50% wt based on dry film weight.

Release of the nitrite anions is by ion-exchange with other anions e.g. the chloride anions of sea water or salt spray and does not, as is normal with corrosion inhibiting coatings, depend on water solubility.

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SPECIFICATION
Corr sion inhibitors and c atings containing them

This invention relates to corrosion inhibitors suitable for incorporation into protective coatings, e.g. paints.

It is well known that certain anions, e.g. phosphate, chromate, nitrite and benzoate anions, have corrosion inhibiting properti s and that compounds containing such sp cies can be included in protective coatings. Th compounds are usually in the form of sparingly water-soluble salts. The coatings themselves have a limited permeability to water and it is believed that the mechanism of corrosion inhibition involves the gradual dissolving of the compounds in water releasing the anions as the active inhibitors. For such systems to be effective over a long period the solubility of the compound is particularly important. If the compound is too soluble, blistering of the coating may occur and the compound will be rapidly depleted; if it is insufficiently soluble the compound will be ineffective.

Although nitrite anions are known to have corrosion inhibiting properties, compounds containing nitrites are not normally used in paints and other protective coatings because they are too soluble in water and so are rapidly depleted and would cause blistering of the coating. Known supports for anions are inorganic oxides such as silica but the strong acid conditions required for ion-exchange with the inorganic oxide break down the nitrite.

The present invention is concerned with nitrite corrosion inhibitors which depend for their effectiveness on ion exchange rather than solubility and which do not require strong acid conditions for their formation.

According to the present invention, a corrosion inhibitor comprises particles of an organic anion-exchange resin having corrosion inhibiting nitrite anions chemically bound to the particles.

Organic anion-exchange resins capable of combining with nitrite anions and available in particle form are known. Thus anion-exchange resins containing basic nitrogen atoms are known. One particular known resin is a divinyl benzene-styrene copolymer which can be chloromethylated and then treated with an amine to introduce basic nitrogen atoms. Commercially available resins of this type are sold under the registered trade marks of, for example, "Amberlite", "Dowex" and "Zerolit".

These resins are normally sold in neutral form with, for example, a chloride anion. They may be converted to corrosion inhibiting resins by ion-exchange with solutions containing nitrite ions. The solutions may be at any suitable pH preferably neutral pH and exchange may be effected by simple percolation of a solution containing a suitable excess of nitrite anions through the resin at ambient temperature. The uptake of the corrosion inhibiting nitrite anions on to the resin can be measured by standard analytical techniques, such as, for example, elution and iodine titration.

The amount of corrosion inhibiting nitrite anions which can be taken up by the resin depends on the ion-exchange capacity of the resin. It has been found that, using the simple percolation techniques previously described, substantially complete exchange can be achieved giving corrosion inhibiting nitrite anion contents of up to 17% weight by weight of anion-exchanged resin.

The corrosion inhibiting particles may be included in protective coatings and the present invention includes protective coatings containing corrosion inhibiting particles as described above. The protective coating may be any of the known types of protective coatings based on film forming polymers or resins, e.g. paints, varnishes and lacquers. It may, in particular, be primer paints based on epoxy resins, vinyl resins, alkyd resins, chlorinated rubbers or cyclised rubbers.

The corrosion inhibiting particles may act as a filler for the coating and may be included in relatively large amounts of up to 50% wt, based on the dry film weight.

When used in protective coatings the particles should be suitably small so as to remain in suspension in the liquid before application and so as not to substantially affect the ease of application or the smoothness of the dry coating. Suitable particle sizes may be up to 30 micron diameter. It has been found that a small particle size is also important in getting effective corrosion inhibition and, if necessary, commercially available resins may be ground to finer particles in air or an inert liquid, e.g. acetone. Thus a coating containing nitrite anion-exchanged particles of a commercial resin of 200—400 mesh BSS particle size gave relatively poor corrosion inhibition. When these anion exchanged particles were ground in acetone to a particle size of 20μm and used in an otherwise identical coating, the corrosion inhibiting properties improved considerably. If grinding is required, the grinding may be applied to the particles either before or after the addition of the corrosion inhibiting ions.

The corrosion inhibiting particles act to release the anions into solution by ion exchange with an anion which exists in the environment in which the particles are used. Thus the invention is particularly useful for protecting structures in or above the sea, the sea providing chloride anions for exchange with the corrosion inhibiting anions. The structures will normally be metal structures and the corrosion inhibiting particles will normally be in a protective coating. Unlike present paints which act by the solubilisation of corrosion inhibiting salts, it is the permeability to the exchanging anions rather than the permeability of water which controls the rate of release of the corrosion inhibiting anions. Thus the corrosion inhibiting anions will be preferentially released from the resin in those areas where the desired barrier properties of the coatings are weakest.

Particular structures which may be protected are the hulls and superstructures of ships, and rigs and platforms used for oil or gas exploration or production.

The invention may, however, have application for protecting structures on land where potentially corrosive ions may be present in the atmosphere. Thus coatings containing corrosion inhibiting nitrite anions may be used to protect structures subject to atmospheres with relatively high concentrations of SO_2, SO_3 or Cl^-.

The invention is illustrated by the following example.

EXAMPLE

50 grams of ion-exchange resin was prepared by exchanging the nitrite anion (NO_2^-) onto Amberlite CG400 (CL) anion exchange resin using 1 litre of a solution of 1 molar sodium nitrite in water at ambient temperature. The product was dried under vacuum and ground in acetone until the particle size was below 30 μm. The ground product was incorporated in coatings as follows:

Paint 1	Paint 2	Paint 3
40g Synolac 76W	40g Synolac 76W	International
0.05g Soya Leicithin	0.05g Soya Leicithin	Zinc Chromate Primer
0.33g 36% Lead Octoate	0.33g 36% Lead Octoate	(Modified Alkyd)
0.1g 12% Cobalt Octoate	0.1g 12% Cobalt Octoate	
0.15g Nuodex Exkin	0.15g Nuodex Exkin	
47.2g TiO_2 Rutile	23.6g TiO_2 Rutile	
	6.75g Nitrite Resin	

The first 5 components of paints 1 and 2 were the normal components of a standard long oil alkyd resin mix. Paint 2 contains the nitrite exchanged resin and paint 1 is a control containing the same volume of inert TiO_2 filler. Paint 3 is a conventional anti-corrosive primer.

The paints were applied as a 65 micron coating to steel panels previously cleaned in an ultrasonic bath and the panels were placed in a British Standard 3900:F2 humidity cabinet (10 days at 100% humidity cycling between 42 and 48°C). The following results were obtained on a scale of 1 to 5, where 1 is very good and 5 is bad:

Paint	Corrosion	Blistering
1	5	1
2	1	1
3	2	1

Paints 1 and 2 were also applied as a 65 micron coating to steel plates previously cleaned in an ultrasonic bath and cured for 7 days at room temperature. The coated panels were then scratched through to the bare metal and subjected to the ASTM B117—73 salt spray test for 330 hours. The rusting of the plates was evaluated according to ASTM D610—68 (without blistering) on a scale of 0 to 10 where 0 is a bad result and 10 is a good result. Paint 1 which did not contain nitrite exchanged resin was badly corroded and had a value of 1. Paint 2 which contained the corrosion inhibitor according to the present invention had a value of 9.

CLAIMS

1. A corrosion inhibitor comprising particles of an organic anion-exchange resin having corrosion inhibiting nitrite anions chemically bound to the particles.

2. A corrosion inhibitor according to claim 1 characterised in that the particles are less than 30μm in diameter.

3. A corrosion inhibitor according to either of claims 1 or 2 characterised in that the particles contain up to 17% weight of nitrite anions by weight of anion-exchange resin.

4. A corrosion inhibitor according to any of claims 1 to 3 characterised in that the organic anion-exchange resin is aminated divinyl benzene-styrene copolymer.

5. A protective coating containing corrosion inhibiting particles as claimed in any of claims 1 to 4.

6. A protective coating as claimed in claim 5 characterised in that it contains up to 50% weight of particles based on the dry film weight.

7. A protective coating as claimed in either of claims 5 or 6 characterised in that the coating is based on epoxy resin, vinyl resin, alkyd resin or chlorinated rubber.

8. A corrosion inhibitor as claimed in claim 1 substantially as described in the Example.

9. A protective coating as claimed in claim 4 substantially as described in the Example.

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